

The role of the reaction medium in the self propagating high temperature synthesis of nanosized tantalum powder

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Abstract

The high temperature combustion of the mixture $\text{Ta}_2\text{O}_5 + 5 \text{ Mg}$ has been investigated using a microthermocouple in the medium MgO and molten NaCl . The effect of varying the amounts of these two inorganic agents (MgO and NaCl) was examined. It was shown that using MgO as the reaction medium produces the complex oxide $\text{Mg}_x\text{Ta}_y\text{O}_z$ as an impurity in the Ta powder, whereas unagglomerated single-phase powder (particle size of 20–90 nm) of Ta was formed in the presence of NaCl . The approximate mechanism for forming the final product is discussed. The distributions of temperature, the rate of heat generation and degree of conversion in the combustion wave of the mixture $\text{Ta}_2\text{O}_5 + 5\text{Mg} + \text{NaCl}$ were measured. The sizes of the combustion zones and the kinetics of reaction were derived. © 2003 The Combustion Institute. All rights reserved.

Keywords: Tantalum powder; Nanosize; Reaction medium

1. Introduction

The reaction medium is one of the most important features of a chemical process. The main parameters characterizing a chemical reaction, such as: temperature, velocity, direction of course, phase composition and morphology of the final product are all connected with the properties and physical condition of the medium. The role of the reaction medium is equally important for chemical processes, which are independent of the physical state of the reacting system (gas, liquid, or solid).

It is well known, that many important compounds are prepared using methods promoting interaction in the solid state, such as furnace technology, mechano-chemistry and self-propagating high-temperature synthesis (SHS) [1–3]. Compared with furnace tech-

nology and mechano-chemistry, SHS is the hottest, fastest, and most attractive scientifically, because the components interact nonisothermally when the heating rate of substances in a wave is $\sim 10^3$ to 10^6 K/s. Of course, under such extreme conditions, when the formation of end-products proceeds by reactive diffusion the role of the reaction medium can become paramount.

In this study, the influence of the reaction medium on the combustion of $\text{Ta}_2\text{O}_5 + \text{Mg}$ and the formation of microstructures were investigated. Combustion was performed in the presence of large amounts of solid MgO and molten NaCl . Interest in the system $\text{Ta}_2\text{O}_5 + \text{Mg}$ was initiated by the importance of tantalum powder in modern engineering. In particular, metallic tantalum has found wide applications in electronics, bioengineering, chemical and mechanical engineering, nuclear power, and metallurgy because of its unique properties such as plasticity, durability, corrosion-stability, refractory properties, high thermal conductivity and small work function [4,5].

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Nomenclature

k	Mole number
L	Thickness
ℓ	Distance
m	Mass speed
n	Exponent in Eq. 6
Q	Heat of reaction
T	Temperature
t	Time
U	Combustion speed

Greek Symbols

$\phi(x)$	Rate of heat generation
$\eta(x)$	Degree of conversion
λ	Thermal conductivity
ρ	Density

Subscripts

ad	Adiabatic
c	Combustion
fin.	Final
in.	Initial
mix	Michaelson zone

Superscript

*	Starting
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2. Experimental

The raw mixture was prepared using tantalum oxide, magnesium, magnesium oxide and sodium chloride powder with the molar composition:



The properties of the reactants were as follows:

1. Tantalum oxide (Ta_2O_5) with particle size 0.5 μm (99.9% purity, High Purity Chemicals Researches Center, Co. LTD, Japan).
2. Magnesium powder, with particle size 100 to 200 μm (98.5% purity, Daejung Chemicals and Metals Co. LTD, Korea).
3. Magnesium oxide (MgO) with particle size <1 μm (99.5% purity, Daejung Chemicals and Metals Co. LTD).
4. Sodium chloride, with particle size <50 μm (99.5% purity, Samchun Pure Chemical, Co. LTD, Korea).

A green mixture of the reactants was homogenized in a ceramic mortar. Then it was stamped in a cylindrical stainless steel mold to 30 mm in diameter and 40 mm in height. Combustion was carried out in a constant pressure reactor under an atmosphere of argon at 5 bar. Experimental details have been described elsewhere [6]. During a typical experiment a pellet was placed into the reactor and combustion was initiated by means of a nickel-chromium wire located on the upper surface of the pellet and was programmed to produce a voltage pulse of 15 to 20 V for ~ 1.0 to 1.5 s. A high-temperature flame propagated spontaneously through all the mixture.

The maximum combustion temperature (T_c) and also the temperature distribution were measured by three tungsten-rhenium thermocouples (W-5%/Re vs. W-20%/Re) 100 and 50 μm in diameter. They had previously been covered with a thin layer of alumina and embedded in the center of the sample at pre-defined distances from each other. The output signals from the thermocouples were transformed by a data logger (DASTC, Keithley) at the rate of 10 Hz, and then recorded by a computer. The average values of combustion speed were calculated as follows: $U_c = \ell / t$, where U_c is combustion speed; ℓ is the distance between thermocouples; t is the time-interval between the signals from the thermocouples. The standard errors of measurement for T_c and U_c were $\pm 25^\circ\text{C}$ and 5%, respectively. The phase composition of the combustion products was determined with an X-ray diffractometer (XRD; Siemens D5000, Germany). The morphology of the products and their particle size were observed using a Field Emission Scanning Electron Microscopy (FESEM, JEOL, Japan) and a Transmission Electron Microscope (TEM).

3. Results and discussion

3.1. Thermodynamics of process

Preliminary thermodynamic calculations for the mixture $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{MgO}$ (or NaCl) were performed to discover the equilibrium temperatures and compositions of the combustion products under adiabatic conditions. This calculation was performed using the program "THERMO" specially developed for combustion processes [7]. Calculation of the equilibrium characteristics was based on minimizing the Gibbs energy. Some results are given in Fig. 1, which shows that the reduction of Ta_2O_5 by magnesium is characterized by high combustion temperatures (2612°C). One would not expect to synthesize ultra-fine tantalum powder at this temperature. Therefore, combustion of this system was considered in the presence of large amounts of powdered MgO and NaCl, which have the capability of reducing the tem-

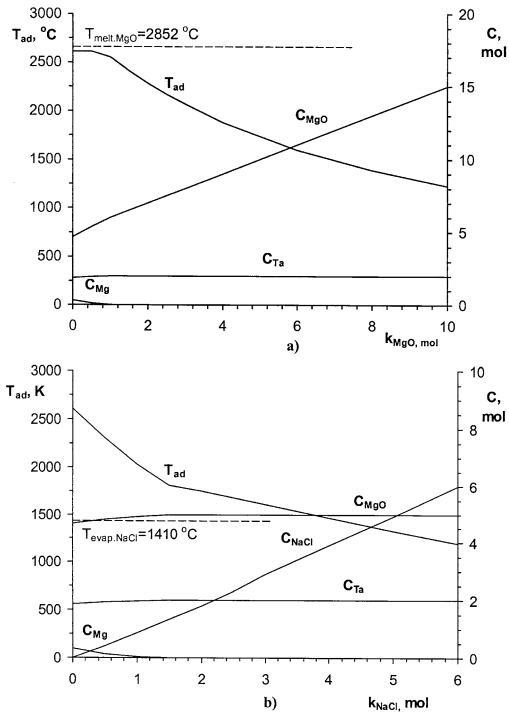


Fig. 1. Thermodynamic analysis of combustion temperature and equilibrium compositions of (a) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{MgO}$ and (b) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{NaCl}$ (b), $P_{\text{Ar}} = 5$ bar.

perature and remaining inert in the reacting system. As can be seen from Fig. 1 increasing k (here k is mole number of inert constituents) monotonically reduces the temperature (T_{ad}). In the case of NaCl, the drop in temperature is much faster (Fig. 1b). In all probability, it is connected with the additional consumption of reaction heat in the melting and evaporation of NaCl. Also one can expect the reaction products are three-phase and don't contain any unexpected substances. It is clear from Fig. 1a that the combustion temperature of the system $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{MgO}$ is always lower than the melting point of MgO. Consequently, the reduction of tantalum will take place in solid MgO. There is a completely different thermodynamic situation in the system $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{NaCl}$, where because of the low melting temperature of NaCl, the reaction is expected to occur in the medium of molten salt. It is natural to suppose that this difference should be a result of different regularities of combustion and the final product forming a microstructure.

3.2. The combustion parameters and morphology of the final product

As was expected, the combustion speed of the green mixture of $\text{Ta}_2\text{O}_5 + 5\text{Mg}$ was very fast; plots

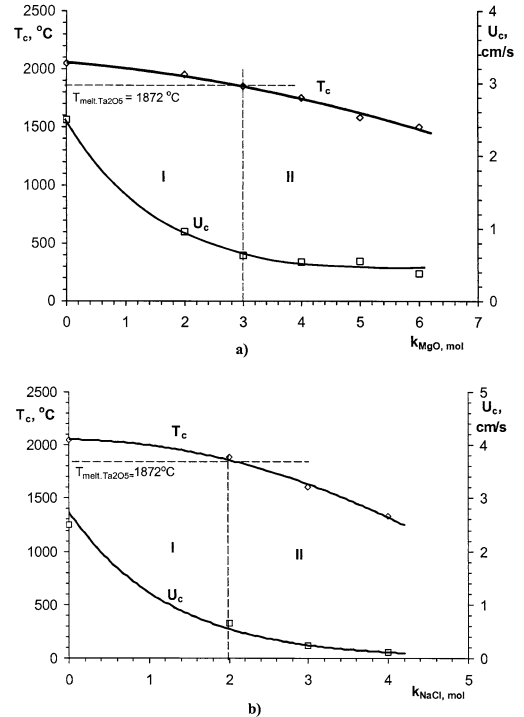


Fig. 2. Dependences T_c and U_c upon k for combustion of (a) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{MgO}$ and (b) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{NaCl}$, $P_{\text{Ar}} = 5$ bar.

of U_c against k are shown in Fig. 2. As a result, an essential part of the green mixture was sprayed into the reaction chamber with a flow of evaporated magnesium. Therefore, the maximum temperature measured in the combustion front was lower ($2050 ^\circ\text{C}$) than the adiabatic combustion temperature ($2612 ^\circ\text{C}$). The use of MgO and NaCl allowed us to gradually decrease the combustion temperature and speed (see Fig. 2a,b) and provide more favorable thermal and diffusion conditions for the formation of final products. Use of these compounds as temperature-decreasing agents and as the reaction medium has been found to be advantageous: MgO has been known for a long time as a 'traditional diluent' in SHS within the reduction stage [8]; NaCl is interesting because of its low melting point and is widely used in preparing tantalum powder [9]. As is visible in Fig. 2a,b the interval of k explored is conditionally divided into two zones: I and II, with the melting point of Ta_2O_5 being the criterion. In Zone I, because of Ta_2O_5 melting, the propagation speed of the combustion wave is fast and can be described by an exponential law. From the practical point of view, Zone II is more interesting; the combustion temperature is moderate and the necessary conditions for controlled combustion exist. In this zone the change of U_c is insignif-

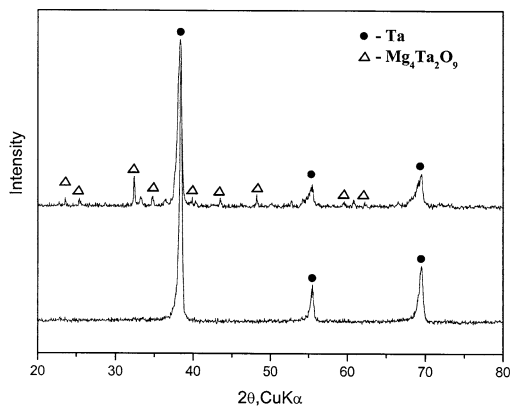


Fig. 3. XRD patterns of tantalum powder prepared from the mixtures: (a) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + 6\text{MgO}$ and (b) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + 3\text{NaCl}$.

icant, which permitted us to estimate what the role of MgO and NaCl is in the reduction of tantalum. As was mentioned above, the final temperature fell on adding MgO or NaCl , because of the heat required to warm-up of these additives.

Typical XRD patterns of the reaction products after acid leaching are given in Fig. 3. As one can see, with the use of MgO as a reaction medium, a rather stable and undesirable $\text{Mg}_4\text{Ta}_2\text{O}_9$ always forms as an impurity (Fig. 3a). In the case of NaCl the formation of secondary phases was not observed and after acid leaching a single-phase of pure tantalum powder was successfully obtained (Fig. 3b).

The formation of the phase $\text{Mg}_4\text{Ta}_2\text{O}_9$ is most likely a result of an interaction between MgO and Ta_2O_5 in the intermediate stages of combustion. Additional experiments with the binary system $\text{Ta}_2\text{O}_5 + \text{kMg}$ at lower k ($k = 0.85\text{--}2.0$) were conducted to reveal how the complex oxide is formed. In particular, the change in temperature and the composition of the phases in the final product is shown in Fig. 4. The composition of the phases was calculated from the appropriate XRD patterns. It is clear that with incomplete reduction, a remaining portion of Ta_2O_5 reacts with the MgO forming the complex oxides $\text{Mg}_x\text{Ta}_y\text{O}_z$. At a low concentration of MgO , the main oxide phase is MgTa_2O_6 . With an increase of k , $\text{Mg}_5\text{Ta}_4\text{O}_{15}$ and $\text{Mg}_4\text{Ta}_2\text{O}_9$ become predominant. The latter was always observed in the synthesis of tantalum in a medium of MgO .

According to FESEM, the tantalum powders synthesized in various reaction media (at $1500\text{--}1600^\circ\text{C}$), despite approximately identical particles sizes ($<0.5\text{ }\mu\text{m}$), differ distinctly in their morphology (see Fig. 5). A comparison of the micrographs shows that tantalum powder prepared in NaCl has a lower de-

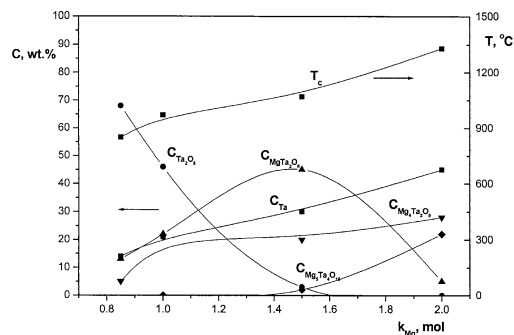


Fig. 4. Combustion temperature and phase composition of final products of combustion of $\text{Ta}_2\text{O}_5 + \text{kMg}$, $P_{\text{Ar}} = 5\text{ bar}$.

gree of agglomeration (Fig. 5b) and a cleaner surface than that prepared in MgO (Fig. 5a). Thus, it is possible to conclude that the cleanliness and morphology of the raw tantalum powder are connected with the chemical nature and physical state of the reaction medium. When the reaction proceeds in a medium of MgO , the preparation of single-phase un-agglomerated powder is complicated, because of the solid state of MgO and its high chemical reactivity with Ta_2O_5 , forming the complex oxide.

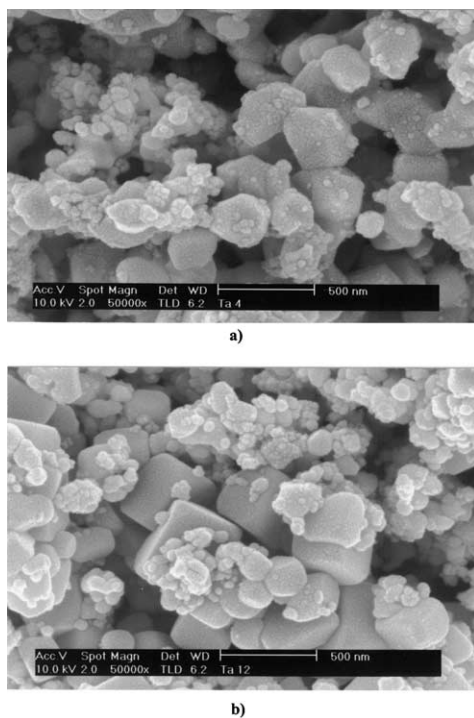


Fig. 5. FESEM micrographs of the Ta powders synthesized from (a) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + 6\text{MgO}$ and (b) $\text{Ta}_2\text{O}_5 + 5\text{Mg} + 3\text{NaCl}$.

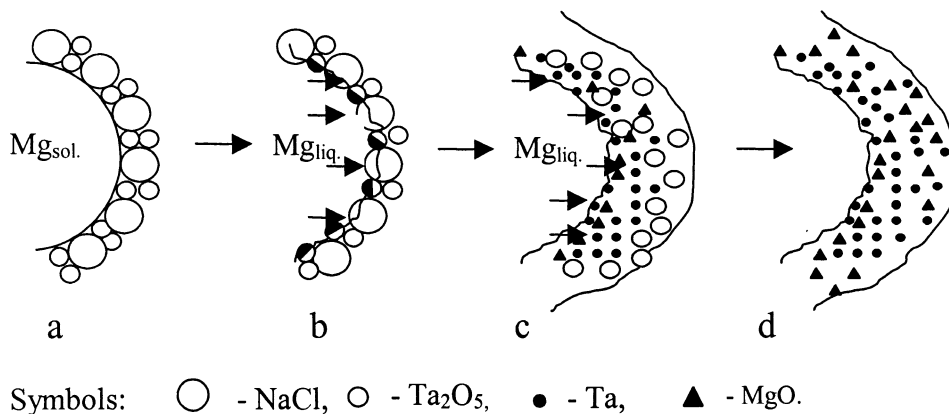
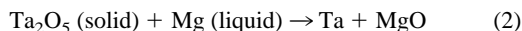


Fig. 6. The scheme for forming tantalum powder in the liquid NaCl: (a) green mixture, (b) Mg melting and beginning of the reaction, (c) the melting of NaCl and particles protection, and (d) final product.

Distinct from MgO, the use of sodium chloride prevents the complex oxide from forming. One simple scheme, which is able to explain this phenomenon is shown schematically in Fig. 6. The initial condition of the green mixture is shown in Fig. 6a: a large particle of magnesium (50–100 μm) is surrounded by smaller particles of NaCl and Ta₂O₅. Combustion begins after the melting of magnesium (this was confirmed through DTA analysis). The state of the system when the reaction has just been initiated and NaCl has not yet begun melting (650–800°C) is represented in Fig. 6b. The black areas show a partial transformation of Ta₂O₅ into Ta. This process can be described by:



Because of the heat generated by reaction (2) the melting of NaCl begins at 810°C. In the span of 1 s all the solid particles appear in the molten salt and the reduction of Ta₂O₅ changes to a reactive diffusion mode (Fig. 6c). From this moment on, all the solid particles will be spatially divided from each other by the molten NaCl and will be kept in this state until the completion of the reaction (Fig. 6d). Moreover, on increasing the concentration of NaCl, the sizes of the tantalum particles monotonously decrease, passing into the nano-sized region. In particular, TEM micrographs of tantalum powder prepared from a mixture Ta₂O₅ + 5Mg + 4NaCl are shown in Fig. 7. The average dispersity of the tantalum powder estimated from the micrograph is ~ 20 to 90 nm. The main part of the particles, as a rule, has a form closer to spherical; they are well separated from each other.

3.3. The macro-kinetic laws of tantalum reduction in the molten NaCl

One of the important tests of solid state combustion is an experimental determination of the temperature distribution in the combustion wave. A great amount of useful information concerning combustion mechanisms can be extrapolated from these distribu-

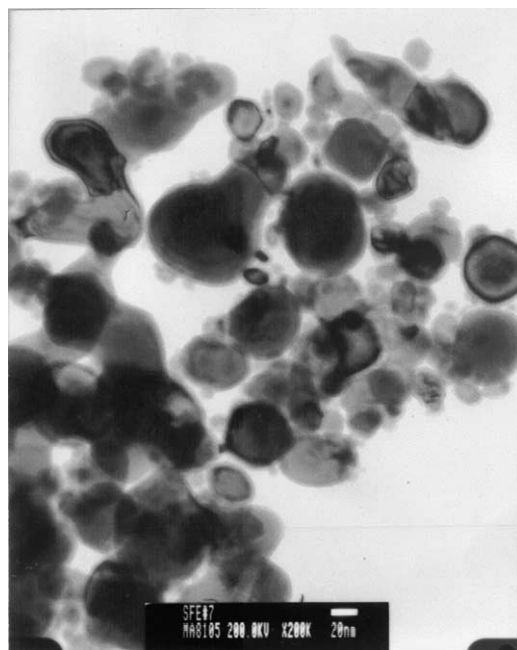


Fig. 7. TEM micrograph of Ta powder prepared from Ta₂O₅ + 5Mg + 4NaCl.

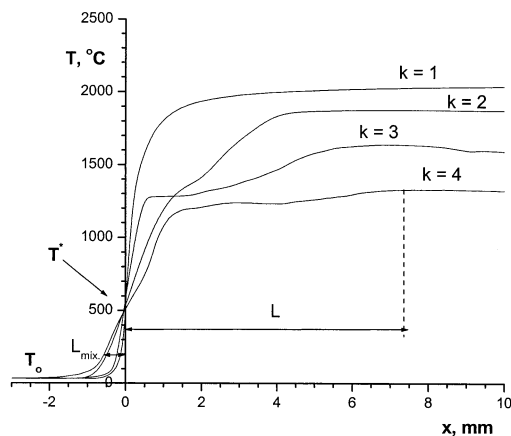


Fig. 8. Average temperature distribution in the combustion zone of $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{NaCl}$: The values of k are as shown.

tions. The temperature distributions in the combustion wave of the mixture $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{NaCl}$ was obtained by a microthermocouple technique [10], using tungsten-rhenium thermocouples 50 μm in diameter and previously covered with a thin alumina layer. This revealed two types of temperature distributions: a single-stage and double-stage (Fig. 8). The single stage temperature distribution was recorded at $k = 0$. Here, T is the current temperature, T^* is the starting temperature of reaction; L_{mix} is the thickness of the pre-flame zone (Michaelson zone) and corresponds to changes in the temperature from T^* up to $T = T_0 + (T^* - T_0)/e$; L is the thickness of the reaction zone and corresponds to changes in the temperature from T^* to T_c . By means of the ordinate, combustion can be separated into two zones, the so-called pre-flame zone (left side) and the chemical conversion, or reaction zone (right side). In the pre-flame zone, intense heat transfer takes place, but a chemical reaction does not. According to the results of DTA analysis, combustion starts at 650°C after melting of the Mg. This temperature was regarded as the starting temperature of the reaction (T^*). With $k = 0$, in the beginning portion of the reaction zone the temperature increases rapidly up to 1750 to 1850°C, and then the long tail of the after-burning zone follows. The isothermal area at a temperature of 1180 to 1430°C registered at $k = 2$ to 4, seems to be connected with the heat consumed in the evaporation of Mg and NaCl ($T_{\text{evap. Mg}} = 1107^\circ\text{C}$, $T_{\text{evap. NaCl}} = 1410^\circ\text{C}$). In these distributions the melting zone of NaCl is not detected easily because of a blocking effect of the combustion temperature. However, it is somewhat visible at $k = 4$. The total size of the reaction zone in Fig. 8 is rather large in comparison with the pre-flame zone. Of particular interest, in all of the investigated

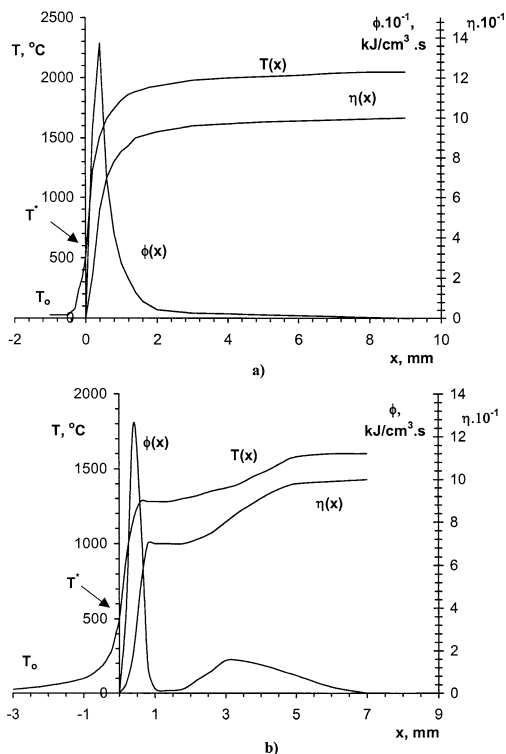


Fig. 9. The distribution of the temperature $T(x)$, degree of conversion $\eta(x)$, and rate of heat generation $\Phi(x)$ in the combustion wave of the $\text{Ta}_2\text{O}_5 + \text{Mg} + k\text{NaCl}$ for (a) $k = 0$ and (b) $k = 3$.

cases, was the relative size of the reaction zone $\Delta \gg 1$ (were $\Delta = L/L_{\text{mix}}$), which specifies the wide chemical reaction zones [10].

By examining the experimental curves of $T(x)$ given in this work and the thermo-physical constants of this system, the rate of heat generation $\phi(x)$ and degree of conversion $\eta(x)$ for the system $\text{Ta}_2\text{O}_5 + 5\text{Mg} + k\text{NaCl}$, at $k = 0, 2, 3$, and 4 were calculated. The macro-kinetic constants of the combustion process were calculated utilizing a method developed formerly [10]. The calculation was carried out using the following equations:

$$\eta = \frac{mc(T - T_0) - \lambda i_{\text{in}} \frac{dT}{dx}}{(\lambda_{\text{in}} - \lambda_{\text{fin}}) \frac{dT}{dx} + Qm} \quad (3)$$

$$\phi = mQ \frac{dT}{dx} \quad (4)$$

Where, Q is the heat of reaction, J/g; $m = \rho U_c$ is the mass speed of combustion; λ_{in} and λ_{fin} are, respectively, the thermal conductivity of the initial mixture

and final product. Typical plots for $\phi(x)$ and $\eta(x)$ are given in Fig. 9. The function $\phi(x)$ has one or two maxima, depending on the type of temperature distribution, and can be seen, the basic heat release occurs near to T^* , to which the sharp peak of $\phi(x)$ corresponds. This area is responsible for the combustion velocity. Using the curves of $\phi(x)$ it is possible to calculate the macro-kinetic constants of the total reaction. The rate of heat generation can be presented [11] as:

$$\phi = QK_o\varphi(\eta)e^{-\frac{E}{RT}} \quad (5)$$

where the kinetic law was calculated by the equation

$$\varphi(\eta) = \frac{1}{\eta^n} e^{-m_o\eta} \quad (6)$$

where n is the order of reaction and m_o is a braking parameter. The processing of experimental measurements by the formula (5) and (6) results in the logarithmic kinetic law for reaction in the combustion zone, at $\eta = 0.2$ to 0.4

$$\phi = QK_o \exp(-m_o\eta)\exp(-1.007 \times 10^4/T) \quad (7)$$

where $n = 0$, $m_o = 8$, $E = 83.7$ kJ/mol. The derived value of the activation energy is an effective one and specifies only the temperature dependence of the rate of heat generation. Through this system the logarithmic law for the rate of heat generation was obtained. The relatively high value of the braking parameter ($m = 8$) indicates a diffusion mechanism for combustion and the production of the final product.

4. Conclusions

1. A thermodynamic analysis for the system $Ta_2O_5 + 5Mg + kMgO$ (or $NaCl$) was performed. The values of adiabatic combustion temperature and equilibrium composition of combustion products were computed.
2. The effects of MgO and $NaCl$ on the maximum temperature and combustion speed, as well as on the final products and their microstructures

were investigated. It was shown that with MgO as the reaction medium, comparatively stable and undesirable $Mg_4Ta_2O_9$ always forms as an impurity, whereas the use of $NaCl$ leads to the formation of single-phase tantalum powders of size 20 to 90 nm.

3. Temperature distributions in the combustion wave of $Ta_2O_5 + 5Mg + kNaCl$ were obtained. It was shown that the combustion zone could have one or two stages. The temperature plateau arising from evaporation of Mg and $NaCl$ divides the stages.
4. The distributions of the rate of heat generation $\phi(x)$ and the degree of conversion $\eta(x)$ of the reaction were obtained at the different k , which allowed us to calculate the macro-kinetics of the processes forming tantalum at $\eta = 0.2$ to 0.4 . The logarithmic kinetic law of heat generation with the braking parameter $m_o = 8$ was obtained.

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